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Local stoichiometry in amorphous supramolecular composites analyzed by solid-state ^{13}C nuclear magnetic resonance

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Solid-state nuclear magnetic resonance (NMR) has been applied to "*amorphous*" active layers consisting of donor-acceptor self-assembled composites in organic solar cells. Several stoichiometric supramolecular complexation states as well as the charge-transfer states are revealed by the solid-state NMR, which have been difficult to access by conventional spectroscopy. The spectra show clear correlation between local self-assembled supramolecular structures and the organic solar cell performances. © *2011 American Institute of Physics*. [doi:10.1063/1.3565237]

Donor-acceptor (D-A) systems have attracted significant interest in supramolecular chemistry as well as organic electronics including organic solar cells (OSCs).[1,2] In particular, fabrication of "*amorphous*" D-A systems is one of the cost-effective approaches to develop highly-efficient, large-area OSCs. In this regard, the characterization of the molecular-level D-A structure is crucial to design high-performance OSCs, however, the details have been unrevealed for such *amorphous* systems.

Solid-state nuclear magnetic resonance (NMR) is a powerful tool for elucidating the structure of disordered or amorphous systems.[3–7] Recent application of solid-state NMR to organic light-emitting materials with disordered structures has disclosed a relationship between the local structure and the light-emitting properties.[8,9] The application to OSCs is also expected to be highly useful to evaluate the D-A structure, as examplifed by Ref. 10. Here, we present solid-state NMR experiments for two supramolecular OSC systems composed of tetraphenylporphyrin-derivatives (TPP) and C_{60}; 3,5-OMeTPP/C_{60} and 3,4,5-OMeTPP/C_{60} composites (Fig. 1). The 3,5-OMeTPP/C_{60} supramolecular composite led to a remarkably high cell performance with an incident photon-to-current efficiency (IPCE) of up to approximately 60%.[11–13] In contrast, additional introduction of methoxy group at 4-position of 3,5-OMeTPP (i.e., 3,4,5-OMeTPP) resulted in a remarkable decrease in the IPCE values ($<10\%$). One of the purposes in this study is to reveal the origin of the difference. From solid-state NMR experiments, we find the existence of several different supramolecular elementary units possessing local stoichiometry between TPP and C_{60} in an amorphous state, as shown below. The quantitative molar ratio and the degree of charge transfers (CTs) for the respective elementary units would have a large impact on the cell performance, which has never been addressed by conventional spectroscopic analyses.

The above two D-A composites were prepared as follows. The TPP and C_{60}, dissolved in toluene, were rapidly injected into acetonitrile. This resulted in the formation of supramolecular composite clusters, TPP/C_{60}. The gently centrifuged and dried clusters were employed for two different solid-state NMR experiments. First experiments, fully-relaxed direct polarization/magic angle spinning ^{13}C NMR experiments *without* ^{1}H dipolar decoupling (DP/MAS/noDD experiments), distinguished the C_{60}'s in different states with quantitative molar ratios. Second experiments, cross polarization (CP)/MAS ^{13}C NMR experiments *without* DD (CP/MAS/noDD experiments), gave information on the spatial proximity of C_{60} and ^{1}H in TPP (see Ref. 14 for more experimental details).

Figure 2(a) shows a DP/MAS/noDD ^{13}C NMR spectrum of pristine C_{60}. A single resonance line appears at 144.1 ppm. In Fig. 2(b), the DP/ and CP/MAS/noDD ^{13}C NMR spectra of 3,5-OMeTPP/C_{60} clusters in the amorphous states are presented in the left and right, respectively. The resonance lines are denoted as **A** to **F**. Compared with the spectrum of pristine C_{60}, the 3,5-OMeTPP/C_{60} clusters display several upfield-shifted resonance lines, **B**–**F**, which indicate the occurrence of molecular-level complexation between 3,5-

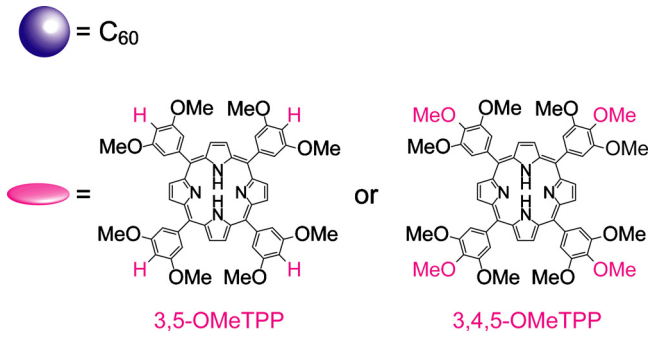

FIG. 1. (Color online) Materials used in this study. (Purple) sphere indicates fullerene (C_{60}). (Pink) disk indicates 5,10,15,20-tetrakis(3,5-dimethoxyphenyl)porphyrin (3,5-OMeTPP) or 5,10,15,20-tetrakis(3,4,5-trimethoxyphenyl)porphyrin (3,4,5-OMeTPP).

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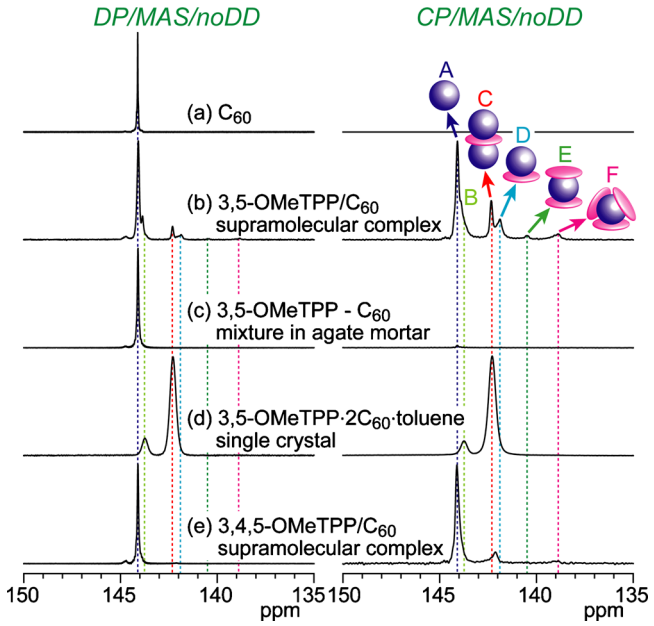

FIG. 2. (Color online) Fully-relaxed DP/MAS/noDD (left) and CP/MAS/noDD (right) ^{13}C NMR spectra of (a) pristine C_{60}, (b) 3,5-OMeTPP/C_{60} supramolecular clusters, (c) 3,5-OMeTPP-C_{60} mixed in agate mortar, (d) 3,5-OMeTPP·2C_{60}·toluene single crystals, and (e) 3,4,5-OMeTPP/C_{60} supramolecular clusters.

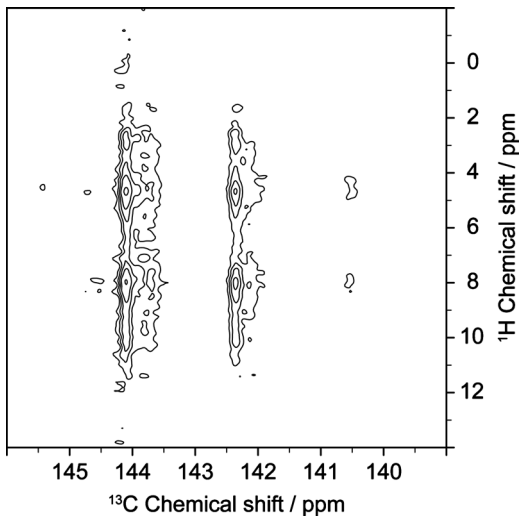

FIG. 3. $^{1}H-^{13}C$ HETCOR spectrum of 3,5-OMeTPP/C_{60} supramolecular clusters without ^{1}H dipolar decoupling during the detection of free induction decay.

OMeTPP and C_{60}. Here, these resonance lines in both the DP/ and CP/MAS/noDD spectra in Fig. 2 do not originate from 3,5-OMeTPP, because the resonance lines of 3,5-OMeTPP are effectively suppressed by not applying DD. This is clearly confirmed by the fact that the NMR spectrum of 3,5-OMeTPP and C_{60} mixture only ground in an agate mortar does not show any detectable upfield resonance lines as shown in Fig. 2(c). Therefore, C_{60} carbons can be selectively detected in all the experiments in Fig. 2. To further confirm the molecular-level complexation, we carried out a two-dimensional (2D) $^{1}H-^{13}C$ heteronuclear correlation (HETCOR) experiment. ^{13}C resonance lines of 3,5-OMeTPP are suppressed by not applying DD as described above and C_{60} does not possess ^{1}H. Therefore, 2D $^{1}H-^{13}C$ HETCOR experiment can show further evidence for the molecular-level complexation. The result, shown in Fig. 3, clearly exhibits the correlation between ^{1}H in 3,5-OMeTPP and ^{13}C in C_{60}.

Our preceding study[11–13] suggests the formation of a single crystal-like structure even in the amorphous sample. Figure 2(d) depicts the DP/ and CP/MAS/noDD ^{13}C NMR spectra of the single crystals, 3,5-OMeTPP·2C_{60}·toluene. A resonance line which emerged at 142.3 ppm in Fig. 2(d) corresponds to the peak **C** in Fig. 2(b). This implies that the elementary unit in the single crystals, consisting of two C_{60} molecules and an intervening single 3,5-OMeTPP molecule,[11–13] really exist in the amorphous sample. Note that a small resonance line, observed at 143.7 ppm in Fig. 2(d), is considered to be C_{60}'s in defects, which are farther from the second neighbors of 3,5-OMeTPP. The ^{13}C chemical shift anisotropy (CSA) NMR measurement on the single crystals [Fig. S1(b)] provides a motionally averaged ^{13}C CSA spectrum, indicating that isotropic rotational motion occurs at a rate larger than the CSA width of ~20 kHz.[15–18] This isotropic rotational motion provides the essentially single resonance line at 142.3 ppm in Fig. 2(d). Otherwise, the resonance lines of the respective carbons in C_{60} should split due to the interaction with 3,5-OMeTPP. The Jahn–Teller distortion was reported for C_{60} in some complex systems.[10,19,20] However, in our case, the x-ray diffraction of the 3,5-OMeTPP·2C_{60}·toluene single crystals did not reveal the distortion.[11–13] Even if the Jahn–Teller distortion takes place, the resonance lines would coalesce into a single line due to the above-mentioned isotropic rotational motion, which is faster than the NMR detection time scale. Therefore, we can safely conclude that the appearance of the several resonance lines in Fig. 2(b) does not stem from the Jahn–Teller effect.

For the 3,5-OMeTPP/C_{60} clusters in Fig. 2(b), signals other than the peak **C** are also observed, showing that the molecular-level structure in the amorphous sample cannot be explained simply by the single crystals structure. Different types of elementary units exist. A host-guest system consisting of C_{60} sandwiched between two porphyrins in Refs. 21–24 is a suitable reference to characterize the structure; C_{60} sandwiched between the two porphyrins exhibits 3.1,[21] 3.6,[22] and 3.4 (Refs. 23 and 24) ppm upfield shift relative to pristine C_{60} in solution ^{13}C NMR. This shift corresponds to the peak **E** in Fig. 2(b). Seemingly sterically-hindered complexation between three 3,5-OMeTPP and one C_{60}, corresponding to peak **F**, is possible as seen in similar systems.[25–27] From these considerations, the peaks **A**, **C**, **E**, and **F** are assigned to free C_{60}, the C_{60} in C_{60}/3,5-OMeTPP/C_{60} unit, the C_{60} in 3,5-OMeTPP/C_{60}/3,5-OMeTPP unit, and C_{60} surrounded by three 3,5-OMeTPP molecules, respectively. Therefore, stoichiometric complexations between 3,5-OMeTPP and C_{60} are responsible for the discrete resonance lines in Fig. 2(b). The peak **D** appears between the two peaks due to supramolecular complexations with the molar ratios of 3,5-OMeTPP: C_{60}=1:2 (peak **C**) and 2:1 (peak **E**), suggesting the stoichiometric composition of 1:1. The upfield shoulder of peak **A** (i.e., peak **B**) can be attributed to C_{60} in the second neighbor of or farther from 3,5-OMeTPP. Although the assignments of **B** and **D** are tentative, the discrete resonance lines reflect the nature of stoichiometric complexations. To confirm the above assignments, we carried out density functional theory (DFT) calcu-

lations for these complexations (the details of the DFT calculations and the results are shown in Ref. 14). The experimental upfield shifts from pristine C_{60}, 1.7, 2.2, 3.6, and 5.1 ppm for the 3,5-OMeTPP/C_{60} supramolecular complexes with molar ratios of 1:2, 1:1, 2:1, and 3:1, respectively, are well reproduced by the DFT calculations for the respective complexes (Table SII, Fig. S2). This also supports the above assignments. A sample in which 3,5-OMeTPP and C_{60} are mixed in a powder form and only ground in an agate mortar exhibits no upfield shifts [Fig. 2(c)]. This unequivocally corroborates that the upfield resonance lines arise from the supramolecular complexation at the molecular level.

The dominant origin of the upfield shifts in the C_{60} resonance lines is CT from porphyrin to C_{60}. This is confirmed by the fact that the ^{13}C resonance lines of 3,5-OMeTPP show downfield shifts on average by complexation with C_{60}; the 3,5-OMeTPP becomes electron-deficient by the CT to form 3,5-OMeTPP$^{\delta+}$. Further supporting evidence for the CT is provided in similar systems in Refs. 21 and 22. The electron-enriched fullerene, $C_{60}^{\delta-}$, is more shielded compared to free C_{60}. Therefore, the peaks **C** to **F** result from four distinctly different degrees of CTs in this system, which would greatly affect the cell performance of the solar cell.

Finally, we compare the difference between 3,5-OMeTPP/C_{60} and 3,4,5-OMeTPP/C_{60} supramolecular self-assembled systems. The quantitative molar ratios of the respective species, **A** to **F**, are obtained from the integrated intensities of the fully-relaxed DP/MAS/noDD resonance lines. The molar ratios of **A**, **B**, **C**, **D**, **E**, and **F** are determined to be 100:22:12:9:1:4 and 100:0:2:0:0:0 for 3,5-OMeTPP/C_{60} and 3,4,5-OMeTPP/C_{60} clusters, respectively. Obviously, the amounts of charge transferred C_{60} are greater for the 3,5-OMeTPP/C_{60} system. Considering that CT plays an important role in the OSCs,[12,13] an increase in molar ratios of the CT complexes exhibiting the larger degree of CTs for 3,5-OMeTPP/C_{60} relative to 3,4,5-OMeTPP/C_{60} system is consistent with the large IPCE value of 3,5-OMeTPP/C_{60}-based cell (about 60%) in comparison with 3,4,5-OMeTPP/C_{60}-based cell ($<10\%$).

Because C_{60} does not have any protons, the CP from ^1H to ^{13}C is not expected, as shown in Figs. 2(a) and 2(c), where no resonance lines are observed for the CP/MAS/noDD spectra. Interestingly, however, resonance lines are unequivocally detected in the CP/MAS/noDD spectra of Figs. 2(b), 2(d), and 2(e), showing the existence of dipolar coupling between ^1H in TPP and ^{13}C in C_{60}. This also demonstrates the formation of supramolecular complexation between TPP and C_{60} in close proximity. The intensities of the CP/MAS/noDD signals in Fig. 2(b) are enhanced by a factor of 1.7, 2.9, 3.3, 3.4, and 3.7 (within ± 0.1) relative to the DP/MAS/noDD for peaks **B**, **C**, **D**, **E**, and **F**, respectively (we define the enhancement factor of free C_{60} as unity). This confirms that the number of the nearest 3,5-OMeTPP molecules around C_{60} increases from **A** to **F**.

In conclusion, we have characterized self-assembled amorphous D-A solids consisting of porphyrin derivatives and C_{60} by solid-state NMR. The DP/MAS/noDD, CP/MAS/noDD, and $^1H-^{13}C$ HETCOR experiments provide molecular-level information on the disordered TPP/C_{60} composites, which explains the remarkable difference in OSC performances arising from subtle structural difference. Such analyses for amorphous solids will become increasingly important in organic electronics as well as in supramolecular chemistry.

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